

151Eu Mössbauer spectroscopic study of the phosphor SrAl₁₂O₁₉:Eu with the magnetoplumbite structure

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¹⁵¹Eu MÖSSBAUER SPECTROSCOPIC STUDY OF
THE PHOSPHOR SrAl₁₂O₁₉:Eu
WITH THE MAGNETOPLUMBITE STRUCTURE

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ABSTRACT The phosphor SrAl₁₂O₁₉:Eu with Eu concentrations from 5% to 100% has been investigated using ¹⁵¹Eu Mössbauer spectroscopy and luminescence measurements. The presence of Eu²⁺ as well as Eu³⁺ ions is shown by both techniques.

The isomer shift belonging to the Eu²⁺ as well as the Eu³⁺ ions slightly increases with increasing Eu concentration, indicating enlarged covalency.

The Mössbauer line width of the Eu²⁺ signal decreases with increasing Eu concentration, which is explained by spin-spin relaxation.

The line width of the Eu³⁺ signal shows a maximum at 25% Eu, which is ascribed to non-equivalent environments due to non-stoichiometry of SrAl₁₂O₁₉. At 25% Eu, the emission spectrum shows an additional band as a consequence of the presence of very small traces of a second phase, and not because of the existence of β-alumina type layers in the magnetoplumbite phase, as suggested in the literature.

MATERIALS INDEX: europium, aluminates, phosphors.

Introduction

Eu-activated materials are known as efficient luminescent materials (1). Eu^{3+} ions show intense characteristic line emissions around 615 nm due to $4f \rightarrow 4f$ transitions, whose energies are only very slightly dependent on the host lattice. $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ is applied as the red-emitting phosphor in fluorescent lamps and projection cathode-ray tubes. Recently, we have reported on investigations of the Eu^{3+} -doped sesquioxides $\text{Ln}_2\text{O}_3:\text{Eu}$ ($\text{Ln} = \text{In, Sc, Y, La, Gd, Lu}$) using ^{151}Eu Mössbauer spectroscopy (2).

Eu^{2+} ions, however, show a broad band emission due to a $4f^{65d} \rightarrow 4f^7$ transition whose position is strongly dependent on the host lattice. In general, Eu^{2+} -activated aluminates are rather efficient phosphors under ultraviolet as well as cathode-ray excitation and are used as the blue-emitting component in fluorescent lamps (3,4). The relation between the crystal structure and the Eu^{2+} luminescence of Eu-activated aluminates with the magnetoplumbite or β -alumina structure is discussed in *Refs. 4 and 5*.

^{151}Eu Mössbauer spectroscopy can yield important information concerning the bonding of the Eu ion in the host lattice. The isomer shift (IS) is proportional to the s -electron density at the Eu nucleus (6), which increases with increasing coordination number, decreasing Eu-O distance and increasing covalency. Using this technique, it is possible to discriminate between Eu^{2+} and Eu^{3+} ions. Due to the additional electron in the inner f -orbitals of Eu^{2+} ($4f^7$) with respect to Eu^{3+} ($4f^6$), the Eu nucleus is more shielded from the electrons in the more outer s -orbitals resulting in a lower value of the isomer shift (about -14 mm/s (6)).

To investigate the dependence of the ratio $\text{Eu}^{2+}/\text{Eu}^{3+}$, the isomer shift (IS) and the line width (Γ) on the Eu concentration, we have studied the well-known phosphor $\text{SrAl}_2\text{O}_9:\text{Eu}$ with the magnetoplumbite structure.

Experimental

All $\text{SrAl}_2\text{O}_9:\text{Eu}$ samples were synthesized with the spray-dry technique. Aqueous solutions of $\text{Sr}(\text{NO}_3)_2$ (prepared from SrCO_3 Merck, p.a.), $\text{Eu}(\text{NO}_3)_3$ prepared from Eu_2O_3 , Rhône-Poulenc, 5N) and $\text{Al}(\text{NO}_3)_3$ (prepared from Al metal, Highways, 5N) were mixed, spray-dried and the powders obtained were fired at 400-500 °C until complete decomposition of the nitrates had occurred. Subsequently, the powders were fired at 1400 °C for 4 hours in a reducing atmosphere (H_2). The Eu concentration was 5, 25, 50, 75 and 100 % with respect to Sr.

All compounds were characterized with respect to phase composition using X-ray diffraction (XRD). The phase homogeneity was studied with electron probe microanalysis (EPMA).

The total Eu content was determined using ICP-emission spectrometry and a complexometric titration with EDTA. This titration was carried out at pH = 5.5 in the presence of acetylacetone to mask the Al.

The Eu^{2+} content was determined using an oxidimetric procedure. In this method the sample was dissolved in HCl solution in the presence of Fe^{3+} ions and with

total exclusion of oxygen from the air. The amount of Fe^{2+} formed due to the reaction of Eu^{2+} with Fe^{3+} was determined by titration with a standard Ce^{4+} solution.

Emission spectra for ultraviolet ($\lambda_{\text{exc}} = 254 \text{ nm}$) as well as cathode-ray excitation were measured at room temperature with standard equipment (see e.g. Ref. 7).

^{151}Eu Mössbauer transmission spectra were recorded with a conventional constant acceleration spectrometer with a 200 mCi ^{151}Sm in SmF_3 source. A proportional counter with 3% CO_2 in Xe was used to detect the 21.6 keV γ -rays. Isomer shifts were calibrated against EuF_3 . The error in the calibration was estimated to be at most 1%, which corresponds to about 0.2 mm/s for an isomer shift of -14 mm/s. The velocity was calibrated using a ^{57}Co in Pd source and an α -iron foil. Each measurement took between a few days and two weeks, depending on the Eu concentration.

For low-temperature measurements the sample was positioned in a helium flow-cryostat. Transmission spectra were obtained in the temperature range between 10 and 300 K.

For analysis of the ^{151}Eu Mössbauer spectra we used a fitting procedure, in which the isomer shift, the quadrupole splitting and the linewidth of Lorentzian profiles are fitting parameters.

Results

All $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$ samples adopted the magnetoplumbite structure. In most samples small traces of $\alpha\text{-Al}_2\text{O}_3$ were detected by X-ray diffraction. The largest amounts of $\alpha\text{-Al}_2\text{O}_3$ were found for the Eu concentration of 25%. At this Eu concentration, also two hardly detectable additional X-ray reflections were observed. For the sample with in-weighed 50% Eu, by chemical analysis an amount of 10.4 wt% Eu_{total} was found, corresponding with 51 mol% Eu. The Eu^{2+} content was determined to be 9.7 wt%.

Emission spectra of $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$ under cathode-ray excitation are shown in Fig. 1. Besides the fact that the intensity below 375 nm is zero as a consequence of the correction procedure, the spectra under ultraviolet excitation ($\lambda_{\text{exc}} = 254 \text{ nm}$) have the same general appearance. They consist of an intense broad-band emission at about 400 nm and very weak line emissions around 600 nm. A second weak emission band around 490 nm was observed very clearly at the Eu concentration of 25% (Fig. 1). It could still be observed, much weaker, at 50% Eu.

^{151}Eu Mössbauer spectra of $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$ with various Eu concentrations are shown in Fig. 2. At about -14 mm/s and about 0 mm/s signals were measured. Data obtained from these ^{151}Eu Mössbauer spectra by fitting them with Lorentzians are given in Table 1. In Fig. 3 ^{151}Eu Mössbauer spectra of $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$ with 50% Eu are shown as a function of the temperature. In the range 10-300 K almost identical spectra were observed for this sample.

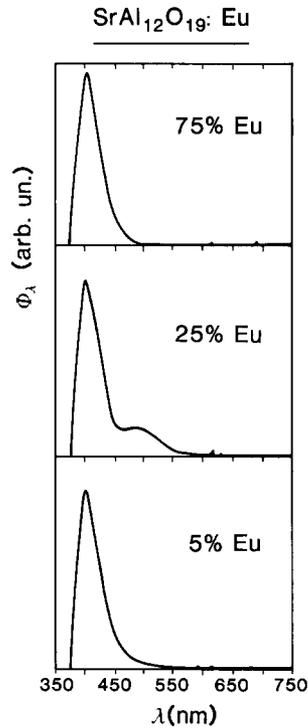


FIG. 1

Emission spectra under cathode-ray excitation of $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$ at room temperature with 5%, 25% and 75% Eu, all with the magnetoplumbite structure.

TABLE I

Isomer shift (IS), line width (Γ), and ratio $\text{Eu}^{3+}/\text{Eu}_{\text{total}}$ obtained from ^{151}Eu Mössbauer spectra of $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$ with the magnetoplumbite structure at room temperature.

Eu conc. (mol%)	Eu^{2+} signal		Eu^{3+} signal		$\text{Eu}^{3+}/\text{Eu}_{\text{total}}$ (%)
	IS (mm/s)	Γ (mm/s)	IS (mm/s)	Γ (mm/s)	
5	-14.3	11.0	-0.4	2.2	9.1
25	-14.2	4.9	-0.3	4.4	5.3
50	-14.2	4.4	-0.1	4.1	5.8
75	-14.1	4.1	0.1	3.1	4.2
100	-14.1	3.6	-0.3	2.5	10.0

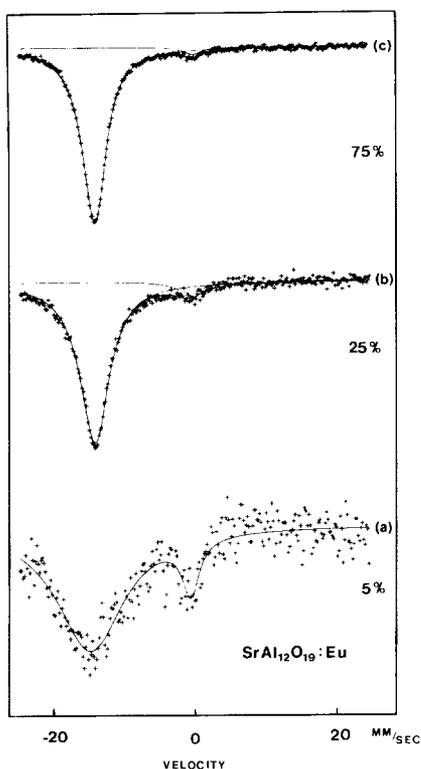


FIG. 2

^{151}Eu Mössbauer spectra of $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$ at room temperature with 5% (a), 25% (b) and 75% (c) Eu, all with the magnetoplumbite structure.

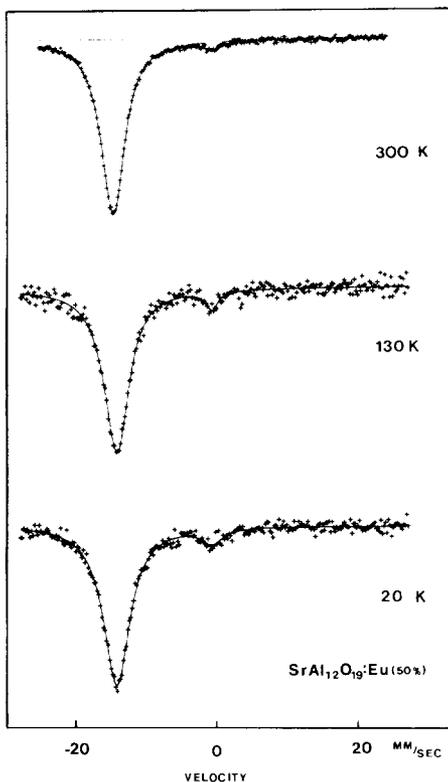


FIG. 3

^{151}Eu Mössbauer spectra of $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$ (50%) with the magnetoplumbite structure as a function of the temperature.

Discussion

For all Eu concentrations, the emission spectra of $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$ (Fig. 1) show an intense broad band with its maximum around 400 nm, originating from Eu^{2+} ions on the Sr site and in agreement with literature data (8). The weak line emissions around 600 nm very probably originate from Eu^{3+} ions in $\text{SrAl}_{12}\text{O}_{19}$, because we have evidence that the Eu^{3+} ions are not located in $\alpha\text{-Al}_2\text{O}_3$ (see below). Unfortunately, no conclusion can be drawn from a comparison with the unclear electroluminescence spectrum of $\alpha\text{-Al}_2\text{O}_3:\text{Eu}$ (9).

A second weak broad emission band was clearly observed around 490 nm for the Eu concentration of 25% (Fig. 1) and also very weakly present at 50% Eu. This wavelength is characteristic for Eu^{2+} emission in the recently described $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}$ (10). The two very weak, hardly observable, X-ray reflections detected at 2.85 Å and 3.20 Å in the X-ray diffractogram of $\text{SrAl}_{12}\text{O}_{19}:\text{25\%Eu}$,

correspond with the strongest reflections of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ (10). Firing this sample at a temperature where $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}$ is no longer stable (*viz.* 1500 °C), leads to the disappearance of the emission band at about 490 nm as well as the additional X-ray reflections. After this firing step, also the reflections of $\alpha\text{-Al}_2\text{O}_3$ were no longer observed, clearly because it has reacted with $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}$ to form $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$. In view of the presence of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}$ in the $\text{SrAl}_{12}\text{O}_{19}:25\%\text{Eu}$ sample, the statement that the extra emission band in the 450-480 nm region in $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$ prepared with a deficiency of Al_2O_3 should be ascribed to Eu^{2+} ions in β -alumina type layers in the magnetoplumbite phase (11), should be reconsidered. Taking the difference in efficiency of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}$ and $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$ a factor 2 for ultraviolet excitation and a factor 3 for cathode-ray excitation (8,10), the amount of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}$ in the $\text{SrAl}_{12}\text{O}_{19}:25\%\text{Eu}$ sample was calculated from the emission spectra to be about 5 wt%. This estimation is in accordance with results of X-ray diffraction and electron probe microanalysis. Moreover, these latter results suggest a lower Eu concentration in $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}$ than in $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$. Because the amount of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}$ was so small, and moreover the Eu concentration is very probably less, the results obtained with ^{151}Eu Mössbauer spectroscopy are not influenced by the presence of traces of this phase.

The emission lines of the Eu^{3+} ions are too weak for changes in position or intensity to be detected at this Eu concentration of 25%, but no clear resemblance with the emission of Eu^{3+} ions in $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}$ could be discerned.

The ^{151}Eu Mössbauer spectra of $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$ (Fig. 2) also show the presence of Eu^{2+} ions (isomer shift around -14 mm/s) and Eu^{3+} ions (isomer shift around 0 mm/s). At high Eu concentrations, the line width of the Eu^{2+} and Eu^{3+} spectra are nearly equal, whereas at low Eu concentrations the line width belonging to the Eu^{2+} ions is much larger. Fig. 4 shows that the isomer shift and the line width of the Eu^{3+} signal as well as of the Eu^{2+} signal do not change as a function of the temperature, as measured for the $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$ sample with 50% Eu.

From the fact that the intensity ratio $\text{Eu}^{2+}/\text{Eu}^{3+}$ is almost temperature independent (Fig. 3), and as a consequence also the ratio $\text{Eu}^{3+}/\text{Eu}_{\text{total}}$ (Fig. 4), we deduce that the temperature dependence of the recoil-free fractions of the Eu^{2+} ions and the Eu^{3+} ions are the same. This means that the recoil-free fractions themselves are the same (12). Therefore the integrated intensities of the signals at about -14 mm/s and 0 mm/s directly yield the relative concentration of Eu^{2+} and Eu^{3+} ions. For low and high in-weighed concentrations, the Eu^{3+} concentration has a maximum value of about 10% of the total Eu concentration, whereas in the intermediate concentration range the Eu^{3+} concentration does not drop below about 4% of the total Eu concentration (Table 1). The Eu^{3+} concentration measured with ^{151}Eu Mössbauer spectroscopy for the sample with 50% Eu ($\text{Eu}^{3+}/\text{Eu}_{\text{total}} = 5.8\% \pm 0.6\%$) agrees quite well with the value determined with chemical analysis ($\text{Eu}^{3+}/\text{Eu}_{\text{total}} = 7\% \pm 2\%$). Clearly the Eu^{3+} concentration is higher for the samples with only regular Sr sites of the magnetoplumbite structure, whereas it decreases for the non-stoichiometric samples.

Fig. 5 shows the dependence of the isomer shift and line width on the Eu concentration for the Eu^{2+} signal.

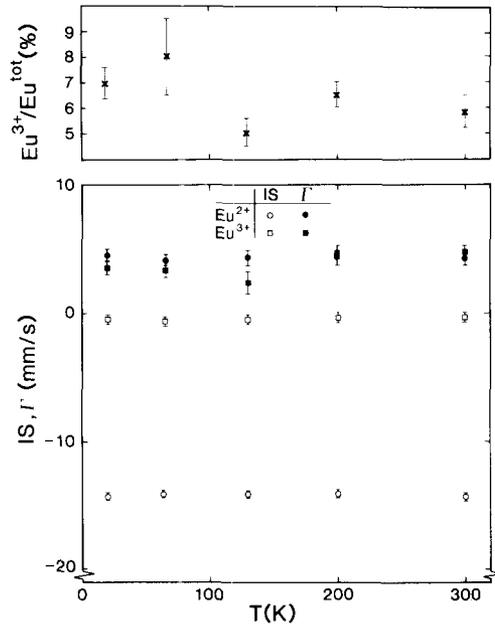


FIG. 4

Area of the Eu^{3+} signal with respect to the total area ($\text{Eu}^{3+}/\text{Eu}_{\text{total}}$), and the isomer shift (IS) and line width (Γ) of the Eu^{3+} and Eu^{2+} ions as a function of the temperature for $\text{SrAl}_{12}\text{O}_{19}:50\% \text{Eu}$.

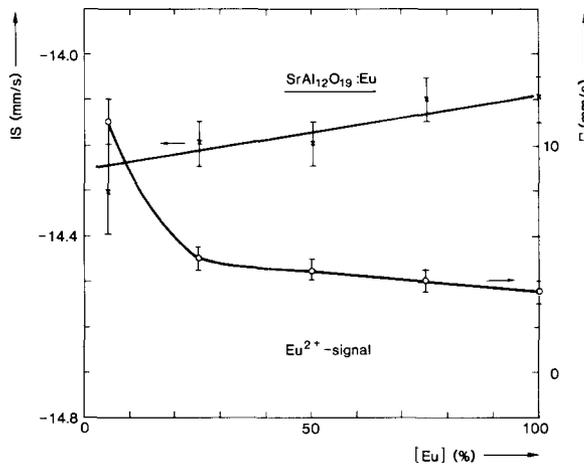


FIG. 5

The isomer shift (IS) and the line width (Γ) belonging to the Eu^{2+} ions in $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$ at room temperature with the magnetoplumbite structure as a function of the Eu concentration.

A free fitting procedure gives an isomer shift of -14.6 mm/s for the sample with 5% Eu. However, because of the bad signal to noise ratio of this spectrum (*Fig. 2*), a relative large variation in the isomer shift of 5% is possible without deteriorating the quality of the fit very much. As we have no plausible reason for a large difference in the isomer shift for low and high Eu-concentrations, we decided to take the from high Eu concentrations extrapolated value of the isomer shift of -14.3 mm/s for the sample with 5% Eu. For increasing Eu concentration, the isomer shift increases slightly to -14.1 mm/s. The Eu-O distance is hardly influenced by the Eu concentration, because the ionic radii of the Eu^{2+} ion and the Sr^{2+} ion are almost the same, which is reflected by insignificant differences between the lattice parameters of $\text{EuAl}_{12}\text{O}_{19}$ and $\text{SrAl}_{12}\text{O}_{19}$. Therefore the small increase in isomer shift of the Eu^{2+} signal indicates an increasing covalency with increasing Eu concentration. This has also been observed for the isomer shift of the Eu^{2+} ions in $\text{LaMgAl}_{11}\text{O}_{19}:\text{Eu}$ with the (distorted) magnetoplumbite structure (IS = -13.5 mm/s for 30% Eu and IS = -13.1 mm/s for 100% Eu (*13*)). The isomer shift as well as the line width of the Eu^{2+} signal do not show peculiarities at 25% Eu, related with the presence of the second type of Eu^{2+} ions, clearly because the lines are so broad and the second phase is only present in very small amounts.

For the purpose of making a comparison between the isomer shift and line width belonging to Eu^{2+} ions in various related aluminate lattices, data are compiled in *Table 2*.

For $\text{BaAl}_{12}\text{O}_{19}:\text{Eu}$ (with Eu-concentrations of 50% and 100%, *i.e.* $\text{EuAl}_{12}\text{O}_{19}$), values of -13.1/-13.3 mm/s are reported for the Eu^{2+} signal (*14*), which is about 1 mm/s higher than we have measured for $\text{EuAl}_{12}\text{O}_{19}$. A comparable difference is found between the values of the Eu^{3+} signal in $\text{EuAl}_{12}\text{O}_{19}$. This suggests differences in isomer shift of the reference sample EuF_3 . Because this is a general problem, discussions concerning the origin of differences in isomer shift of the Eu^{2+} signal between Eu-doped magnetoplumbites and β -aluminas remain speculative. The low isomer shift of -14.6 mm/s, reported for $\text{NaAl}_{11}\text{O}_{17}:\text{Eu}$ besides that of -13.1 mm/s, is attributed to Eu^{2+} ions on a very large site (B site) (*15*).

As can also be seen from *Fig. 5*, the line width significantly decreases from 11.0 mm/s at 5% Eu to 3.6 mm/s at 100% Eu. The line of the sample with 100% Eu may be broadened somewhat from unresolved quadrupole splitting. Absence of hyperfine splitting in this spectrum makes it difficult to correct for the quadrupole splitting. Therefore this splitting is incorporated in the line width. Because the structure of $\text{EuAl}_{12}\text{O}_{19}$ (*i.e.* 100% Eu) and $\text{SrAl}_{12}\text{O}_{19}$ are identical (*5*), the increase in the line width of the Eu^{2+} signal of $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$ with low Eu concentrations cannot be ascribed to contributions of quadrupole splitting due to a change in site symmetry. The additional line broadening of the Eu^{2+} line with decreasing Eu concentration is also seen for other Eu-doped aluminates and ascribed to paramagnetic relaxation effects (*13,14,16*). Evidence for spin-spin relaxation comes from the temperature independence of the line width.

The line width of the Eu^{2+} signal seems to be somewhat larger for the β -aluminas than for the magnetoplumbites. The dependence on the Eu concentration is similar for both aluminates (*Fig. 6*).

TABLE 2

Isomer shift (IS) and line width (Γ) of the Eu^{2+} signal and the Eu^{3+} signal for different Eu-activated aluminate phosphors with respect to EuF_3 .

Compound	Eu conc. (mol%)	Eu^{2+} signal		Eu^{3+} signal		Ref.
		IS (mm/s)	Γ (mm/s)	IS (mm/s)	Γ (mm/s)	
<i>Magnetoplumbite</i>						
$\text{LaMgAl}_{11}\text{O}_{19}:\text{Eu}$	30	$\sim -13.5^{1)}$	$\sim 10^{1)}$	-0.28	2.2	13
	100	-	-	-0.19	2.6	
	100	-13.1	5.6	-0.35	2.3	
$\text{BaAl}_{12}\text{O}_{19}:\text{Eu}^{2)}$	50	-13.3	4.1	-	-	14
	100	-13.3	3.7	0.50	3.2	
	100	-13.1	3.7	0.29	3.2	
<i>β-Alumina</i>						
$\text{NaAl}_{11}\text{O}_{17}:\text{Eu}$ - site A - site B - ³⁾	?	-13.1	3.5	-	-	15
		-14.6	7.8	-	-	
		-	-	~ -1.3	~ 3	
$\text{BaMgAl}_{11}\text{O}_{18.5}:\text{Eu}^{3)}$	10	-	-	-0.18	2.3	14
	50	-13.8	5.8	-0.13	3.8	
	50	-13.4	5.2	-0.30	2.4	
	50	-13.7	6.4	-0.22	5.8	
	75	-13.3	4.9	-0.18	2.3	
	100	-13.4	4.6	-0.03	2.7	
100	-13.5	4.7	0.03	3.0		

1) Determined from figure published in cited reference.

2) Although $\text{BaAl}_{12}\text{O}_{19}$ does not exist with this composition and with the magnetoplumbite structure (3), $\text{EuAl}_{12}\text{O}_{19}$ has the magnetoplumbite structure (5) and the same we assume for $\text{BaAl}_{12}\text{O}_{19}:\text{Eu}$.

3) Formula deduced from data of Ref. 14.

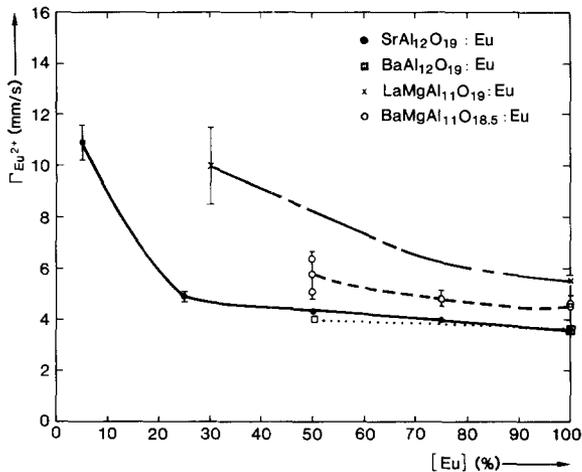


FIG. 6

Line width (Γ) of the ^{151}Eu Mössbauer line belonging to the Eu^{2+} signal as a function of the Eu concentration for different Eu-activated aluminate phosphors with the magnetoplumbite or β -alumina structure.

When comparing line widths in Eu^{2+} -activated magnetoplumbites and β -aluminas, we have to realize that there is a smaller average distance between Eu ions at the same total Eu concentration in magnetoplumbites than in β -aluminas as a consequence of a smaller unit cell of the first materials (5), possibly resulting in a slower paramagnetic spin relaxation and thus a larger line width for Eu^{2+} -doped β -aluminas. Another reason for the larger line width of the Eu^{2+} signal in β -aluminas may be the larger asymmetry of the divalent lattice site in comparison with that of the divalent site in magnetoplumbites (3).

The isomer shift and line width belonging to the Eu^{3+} ions are plotted in Fig. 7 as a function of the Eu concentration.

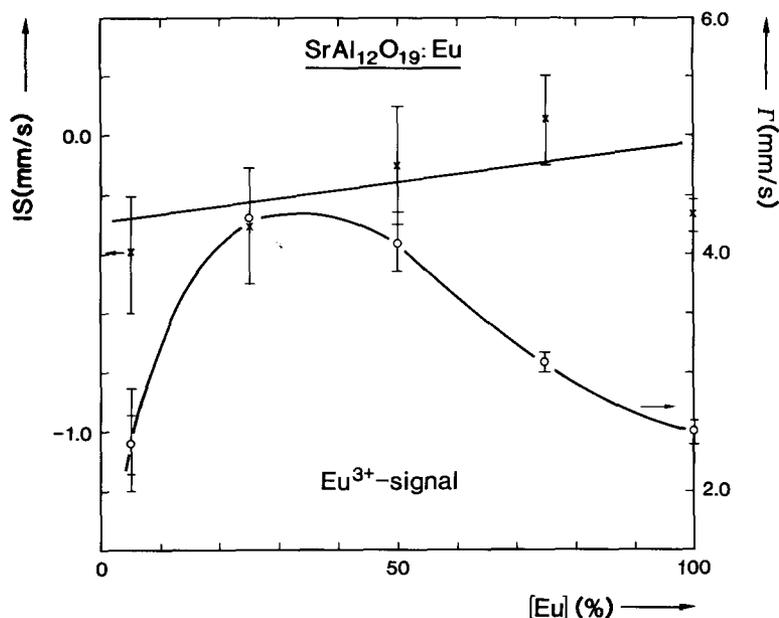


FIG. 7

The isomer shift (IS) and the line width (Γ) belonging to the Eu^{3+} ions in $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$ with the magnetoplumbite structure as a function of the Eu concentration at room temperature.

The isomer shift ranges from about -0.4 to 0.1 mm/s. The possibility that this signal originates from Eu^{3+} ions incorporated in $\alpha\text{-Al}_2\text{O}_3$, which was detected with X-ray diffraction to be sometimes present in small amounts, is very improbable for the following reasons:

1. The amount of rare earth ions, which can be substitutionally incorporated in α -Al₂O₃ is very low: for α -Al₂O₃:Gd a maximum concentration of 0.02% was determined using paramagnetic resonance (17), while we have measured a Eu-concentration of 0.09% in α -Al₂O₃:Eu for which reflections of EuAlO₃ could just be detected in the X-ray diffractogram.
2. We have measured the isomer shift and line width of Eu³⁺ ions in an α -Al₂O₃:0.09%Eu sample to be 0.35 mm/s and 2.93 mm/s, respectively, which deviate significantly from the values we have determined for the Eu³⁺ signal of SrAl₁₂O₁₉:Eu.
3. The deviation between the Eu³⁺ signals in SrAl₁₂O₁₉:Eu and α -Al₂O₃:Eu has no connection with the amount of α -Al₂O₃, as estimated from the X-ray diffractograms.
4. The relative concentration of Eu³⁺ ions and Eu²⁺ ions, as determined from the ¹⁵¹Eu Mössbauer spectrum, is not related to the amount of α -Al₂O₃.

The isomer shift of the Eu³⁺ ions in SrAl₁₂O₁₉:Eu being smaller than 0 is peculiar because for most materials isomer shifts larger than 0 with respect to the ionogenic EuF₃ are found. Assuming that Eu³⁺ substitutes on the Sr²⁺ site, this very low isomer shift is explained by the fact that the Eu³⁺-O²⁻ bond is rather long in this lattice due to the considerably smaller ionic radius of the Eu³⁺ ion (0.95 Å) with respect to the Sr²⁺ ion (1.18 Å). In related Eu-doped aluminate host lattices also an unusual small isomer shift belonging to the Eu³⁺ ions (mostly smaller than 0) was found (Table 2). We ascribe this generally to the quite long Eu³⁺-O²⁻ distance for the small Eu³⁺ ion substituted on a large cation site (ionic radius of Na⁺ = 1.02 Å, Ba²⁺ = 1.35 Å and La³⁺ = 1.03 Å).

As found for the Eu²⁺ signal, a slight upwards trend of the isomer shift of the Eu³⁺ signal in SrAl₁₂O₁₉:Eu with increasing Eu concentration can be observed (Fig. 7). Because we have already seen that the lattice volume does not change significantly with varying Eu concentration, the Eu³⁺-O²⁻ distance remains nearly the same. So we have to conclude that the host lattice becomes somewhat more covalent with increasing Eu concentration, as was found earlier by us for Y₂O₃:Eu (2) and Y₂WO₆:Eu (18).

Because SrAl₁₂O₁₉:25%Eu is not stoichiometric, there is no well-defined identical environment of all Eu³⁺ ions, but a certain variation. This is nicely reflected in the large line width at this Eu concentration of 25%, and also at 50%.

At low and high Eu concentrations, the line width of the Eu³⁺ signal is approximately the same (Fig. 7). This line width is about 2.5 mm/s, which is in the same range as found for the the Eu³⁺ signal in related aluminate host lattices (Table 2). Only for BaMgAl₁₁O_{18.5}:Eu with 50% Eu a significantly larger line width (3.8 and 5.8 mm/s) belonging to the Eu³⁺ signal has been reported (14), which may indicate the presence of a similar phenomenon as found by us for SrAl₁₂O₁₉:Eu.

Conclusion

Luminescence measurements show the presence of Eu^{2+} ions (band emission) and Eu^{3+} ions (line emission) in $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$ with the magnetoplumbite structure. Especially at 25% Eu, an additional emission band was observed, attributed to Eu^{2+} ions in $\text{Sr}_4\text{Al}_4\text{O}_{25}$ in very small amounts.

Using ^{151}Eu Mössbauer spectroscopy the presence of Eu^{2+} ions (isomer shift of about -14 mm/s) and Eu^{3+} ions (isomer shift of about 0 mm/s) was also proved.

Moreover the relative concentration of Eu^{2+} and Eu^{3+} ions in $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$ was determined in a nondestructive way, the results of which are in good agreement with chemical analysis. The $\text{Eu}^{3+}/\text{Eu}_{\text{total}}$ ratio is in between 4% and 10%, depending on the total Eu concentration.

With respect to comparable Eu-doped aluminates, the isomer shifts of the Eu^{2+} signal and the Eu^{3+} signal are in the same region. The low value of the isomer shift of the Eu^{3+} signal is a consequence of the quite long $\text{Eu}^{3+}-\text{O}^{2-}$ distance in these lattices. The isomer shift of the Eu^{3+} signal as well as the Eu^{2+} signal slightly increase for higher Eu concentrations, indicating an enlarged covalency.

The line width of the Eu^{2+} signal decreases significantly with increasing Eu concentration, as also found for comparable Eu-doped aluminates. This is explained by an enhanced spin-spin relaxation as supported by temperature-dependent measurements at $\text{SrAl}_{12}\text{O}_{19}:\text{Eu}$.

The line width of the Eu^{3+} signal shows a maximum at 25% Eu ascribed to non-equivalent environments due to non-stoichiometry of $\text{SrAl}_{12}\text{O}_{19}$ as a consequence of the presence of very small traces of $\text{Sr}_4\text{Al}_4\text{O}_{25}:\text{Eu}$ at this Eu concentration.

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